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FEASIBILITY SURVEY OF ZIRCONIUM AND ALTERNATE REACTOR STRUCTURAL MATERIALS FOR HIGH TEMPERATURE OPERATION

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INTRODUCTION

The selection of metals or alloys to be used as in-pile structural materials depends on a combination of the physical, mechanical, chemical, and nuclear properties of these metals and alloys. Meaningful evaluation of some specific metal or its alloys, such as zirconium, requires comparison with other candidate materials to indicate the specific advantages or disadvantages of zirconium adequately; therefore, this report is not limited to the important properties of zirconium alone, but also lists the properties of some iron and aluminum base alloys.

Certain criteria limit the materials that can be used in a power reactor. Such factors as the type and temperature of moderator, pressure, maximum temperature, and purity of the coolant, and the overall neutron economy must be considered in determining if a material is satisfactory engineering and economics wise.

Limiting criteria assumed in this report are: graphite moderator, to operate at about 500-600 C (930-1100 F); high purity water with adequate pH control at a maximum temperature of 230-300 C (450-570 F) at pressures sufficiently high to prevent the formation of steam and to compensate for the pressure drop throughout the system. This means pressures as high as 1500 psi may be of interest since the saturation pressure for 300 C (570 F) is 1250 psi. Slight enrichment was assumed available, the optimum degree depending on a number of nuclear physical factors. For example, an economic evaluation will be necessary to determine if enrichment is feasible to permit consideration of relatively inexpensive materials having capture cross sections of 2 to 5 barns.

The structural materials considered are limited to those which appear to be satisfactory for jackets and tubes. This does not mean that the materials are limited to these uses, but it is believed that jackets and tubes are critical assemblies and a metal fulfilling the requirements for these will prove satisfactory elsewhere in-pile.

Factors determining the selection of materials for tubes and jackets can be classified by areas. For example, in the 100 Area, such mechanical properties as high temperature tensile and yield strength, ductility, and creep must be known to evaluate candidate tube materials. Similarly the coefficient of thermal expansion and the thermal conductivity are important physical properties. Neutron economy is essential so the macroscopic cross sections and thermal utilizations must be evaluated. Finally, both aqueous corrosion and gaseous oxidation must be considered since excessive rates of corrosion or oxidation may eliminate an otherwise desirable material.

In the case of jackets, closure, neutron economy, corrosion, and heat transfer are of importance. Since the can must serve as a barrier to the surrounding medium to prevent attack of the fuel element, an effective closure by welding, brazing, or some similar method is essential. The material must not corrode too rapidly or selectively at the weld or along the grain boundaries to the degree that penetration and exposure of the fuel element occurs. A satisfactory bond should exist between the fuel element and the jacket, permitting the uninterrupted transfer of heat at this interface without the formation of localized hot spots. This may be done by the formation of a diffusion interface during canning or by a mechanically bonded juncture.

Problems in the 200 Area are predominantly chemical and economic. Should the jacket

material be dissolved together with the fuel or should the jackets remain undissolved because of complications in the various chemical stages due to the presence of stainless steel or zirconium? Is the radiation level too high to permit the handling of the jacket material in the dissolved or undissolved states without specialized and very expensive equipment? Is the jacket material sufficiently valuable to warrant recovery requiring storage in slurry or solid form for a matter of years until the radiation level is sufficiently low to permit refabrication, which would result in a storage and inventory problem? These are believed to be the important issues in the 200 Area.

300 Area problems deal with the fabrication of the tubes and jackets and the canning of the fuel elements. The most satisfactory method of producing the tubes must be determined concomitant with design specifications and cost. The most satisfactory method of canning must be selected on the basis of 100 Area performance, potential reliability, inspection techniques, and cost. The development of these procedures, and an analysis of the methods to select the most desirable are 300 Area problems.

The engineering design of the reactor and an economic analysis of the structural materials fall within the province of the 700 Area. Since the design covers both the reactor and all external equipment, such factors as the influence of water quality on dissimilar materials in and out of the pile, the selection of these materials on the basis of mechanical properties, and the evaluation of these properties to determine if the materials will fit into a reactor, an over-all economic balance of the cost of the structural materials are all 700 Area problems.

By a comparison of the problems existing in the 100, 200, 300, and 700 Areas, the advantages and disadvantages of zirconium compared to aluminum or steel alloys should be apparent. An evaluation of these advantages and disadvantages should permit the selection of the most logical materials for tubes and jackets.

SUMMARY AND CONCLUSIONS

Tube Materials

The three materials, zirconium, aluminum, and steel, can be compared on the basis of 100, 200, 300, and 700 Area problems. Zirconium or Zircaloy-2 appears to be the most satisfactory material for tubes in a high temperature high pressure reactor. Its mechanical properties such as creep resistance and tensile properties are good; its physical properties such as thermal conductivity and coefficient of thermal expansion are adequate. Aqueous corrosion does not appear to be a problem in the temperature range 200-300 C with an alloy such as Zircaloy-2. Gaseous corrosion or oxidation may have to be controlled by adjusting the atmosphere. At present, the data are insufficient to evaluate this factor. The macroscopic cross sections of the zirconium alloys are excellent. Tubes of Zircaloy-2 are better from the standpoint of neutron economy than are those of aluminum. There appears to be no fabrication problems in making tubes, but the effect of extensive cold work on the corrosion resistance must be evaluated further. The material is expensive, but the favorable neutron economy and the relatively long life of the tubes, provided corrosion rates can be controlled, result in a reasonable annual cost.

Insufficient information is available on SAP (sintered aluminum powder) to evaluate this material for tubes. The mechanical and physical properties are undoubtedly

adequate, but nothing is known of the high temperature corrosion resistance in water or pile atmospheres. The macroscopic cross section is very good. Fabrication problems will be greater than for zirconium, and it is not certain that the tubes can be flanged. Present techniques do not permit the welding or joining of SAP by any of the known methods. The cost of this material will be high, but should be substantially less than zirconium.

Stainless steel tubes are eliminated because of the excessive macroscopic capture cross section; all other properties are favorable, but the degree of enrichment required is believed to be intolerable for a thermal reactor.

JACKET MATERIALS

For jackets, zirconium is very expensive, assuming no recovery, and even with recovery this is true due to high fabrication costs, canning costs, and inventory. If a simple cold sized jacket is feasible, the cost will be substantially less than with the more elaborate canning methods. No major closure difficulties are visualized. There may be some problems in separation, particularly if recovery is required. The canning with zirconium is still an unsolved problem as are the separations and recovery problems.

Aluminum as a jacket material poses no problems providing it has sufficient corrosion resistance for the quality of water selected at the desired temperatures. Present work, which is still somewhat preliminary, indicates that there is a definite possibility that aluminum will be satisfactory in the range 200-300 C with adequate pH control and sufficiently pure water. The presence of zirconium tubes may minimize the corrosion of aluminum jackets without extensive pH control. Aluminum should be the least expensive material to use, and should result in no additional 100, 200, 300, or 700 Area problems.

Stainless steel is undesirable as a jacket material due to low neutron economy. The macroscopic cross section of stainless is about 25 times as great as that of zirconium so a jacket of about 0.015-inches still results in a definite decrease in reactivity compared to a 0.030-inch zirconium jacket. Little is known of the canning techniques or the 200 Area problems if stainless steel is used. One definite drawback is the fact that solution of the jacket would mean some redesign since stainless steel is used in the dissolving vessels. Jacket removal would require special and potentially expensive equipment if a method of cracking the jackets was used.

An examination of the properties of the materials considered indicates that Zircaloy-2 tubes are the most feasible on the basis of known mechanical, physical, chemical, and nuclear properties. The only drawback is cost, and this is not excessive if, as anticipated, the gaseous corrosion rate is not too great. On the basis of present information 2S aluminum jackets appear to be feasible. Their availability, cost, physical properties, capture cross sections, and advantages in 200 Area processes are obvious. Existing corrosion data indicate there is a definite possibility that corrosion will not be a limiting factor even without pH control. Zirconium jackets are the suggested alternate, but a great deal of development work is believed to be required before a satisfactory canning procedure is developed. The disadvantages of stainless steel jackets are believed to be greater than the lower material cost, and such a savings is only a minor item since fabrication, canning, enrichment, and decanning represent the principal costs.

DISCUSSION

100 AREA

A material to be satisfactory within the pile must have adequate physical and mechanical properties; it must not fail because of excessive corrosion rates, and the neutron capture cross sections should not be so high that excessive enrichment is required to retain sufficient reactivity. These problems are considered in this section.

Materials to be compared have been limited to Zircaloy-2, sponge zirconium, SAP (sintered aluminum powder), a high strength aluminum-magnesium alloy, 2S aluminum, 347 stainless steel, and 1020 steel. Crystal bar zirconium was not considered because of its high cost relative to sponge zirconium, and because the Zircaloy-2 had better mechanical properties, a good macroscopic cross section, and adequate corrosion resistance.

Physical and Mechanical Properties

The available physical and mechanical properties of the candidate materials will be shown and discussed to determine their comparative qualities under the specified operating conditions.

Physical Properties

The physical constants and some physical properties are shown in Table I. Specfic data for Zircaloy-2 and some of the aluminum alloys are not available, but these would not be expected to differ appreciably from the values shown for zirconium and aluminum.

Tensile Properties

The mechanical strength is one of the governing factors in the selection of the tube material and specification of its required thickness for operation at elevated temperatures. Ductility, and to a lesser extent strength, are also required for the jacket material.

The room temperature and elevated temperature, short-time tensile test data are shown in Tables II, III, IV, V, VI, and VII. The ultimate and yield strengths of the various materials are compared in Figures 1 and 2.

The strength of the aluminum-aluminum oxide alloys increases markedly with increase in oxide content as seen in Table II. They are relatively brittle at elevated temperatures and the ductility decreases as the temperature is raised. The yield strengths of the 7.8 and 16.5 per cent Al_2O_3 alloys at 600 F (315 C) are higher than unalloyed Bureau of Mines zirconium and the Al-6 per cent Mg alloys. At this temperature, 347 stainless steel and Zircaloy-2 (with the standardizing treatment given in Table VI) have approximately the same yield strength and are the best, in this regard, of the materials compared.

The hydrogen embrittlement of zirconium and zirconium alloys observed in impact tests is not noted in tensile tests of Zircaloy-2 without hydrogen solution treatment (Tables VI and VII, or in notched-bar tensile tests even at very low temperatures Table VII). Appreciable ductility is retained in this alloy at low temperatures and notch-strengthening rather than weakening occurs. Late work on the effect of hydrogen content on mechanical properties indicates that concentrations of 120 ppm are necessary to affect the elongation or reduction in area.[32] The impact properties are much more sensitive, with some change observed at contents as low as 46 ppm.

TABLE I

PHYSICAL CONSTANTS

	AISI 347 Stainless Steel (1)*	Aluminum (1)	Zirconium (1)	SAP (10-13 per cent) Al_2O_3 (2)
MELTING POINT °F	2550 - 2600	1220	3380 ± 10	1220 - 1500
Density - g/cm^3	7.98	2.70	6.50	2.8
Electrical Resistivity u ohm-cm	Temp. F. 68 72 752 100 1472 121	Temp. F. 32 2.63 68 2.66 212 3.86 750 8.0	Temp. F. 77 43.9 ± 0.3 212 58 390 73 570 90	Temp. F. 68 Approx. 3.4
Coefficient of Thermal Expansion 10^{-6} in/in/°C	212 16.5 316 18.0 1832 20.0	68-212 23.8 68-390 24.7 68-750 26.7 68-1110 28.7	75 F - Rolled and annealed Thickness 6.7 to 10.1 Transverse 4.8 to 6.3 Longitudinal 4.6 to 5.9	68-212 approx. 19.0
Thermal Conductivity cal/(cm)(sec)(°C)	212 0.037 930 0.052	70 0.503 212 0.503 390 0.530 750 0.546	75 Zr 0.051 75 Zr-5% Sn 0.0228	70 approx 0.4
Macroscopic cross section $\Sigma\, cm^{-1}$	0.23	2S Al - 0.013 A54S0 - 0.012	Zr 0.0077 Zr + 100 ppm Hf 0.0080 Zr + 200 ppm Hf 0.0083 Zircaloy 2 0.0082 Zircaloy 2 + 100 ppm Hf 0.0084 Zircaloy 2 + 200 ppm Hf 0.0087	7.8% Al_2O_3 (3) 0.010

* numbers in parenthesis refer to references

TABLE II

TENSILE PROPERTIES OF ALUMINUM AND ALUMINUM ALLOYS

Material	Heat Treatment*	Test Temperature °F	0.2% Yield Strength psi	Ultimate Strength psi	Elongation % in 2 in.	Modulus of Elasticity 10^6 psi
2S-0 (1)		Room	5000	12000	41 - 45	10
		400	3000	7000	-	
		600	2000	2500		
					% in 10 d	
SAP (2)		Room	34000	48400	6 - 8	
(10-13% Al_2O_3)		300	27000	33000	5	
		600	20000	21000	4	
					% in 4 d	
SAP (3)		Room	17600	22600	22	
(0.5% Al_2O_3)		300	13600	15400	22	
SAP (3)		Room	25000	38000	14	
(7.8% Al_2O_3)		400	18000	21000	-	
		500	16500	18000	-	
		600	14500	16500	13	
SAP (3)		Room	35000	54000	5	
(16.5% Al_2O_3)		400	28000	34000		
		500	24500	28000		
		600	21000	23000	4	
A54S0 (33)		300	15000	35000		
		600	5000	9500		
A5980 (4)					% in 2-in.	
Al-6% Mg	HST-1	Room	27200	49775	22.5	
0.51% Cr	HST-1	600	-	11200	63.0	
0.09% Ti	HTAS-1	Room	27425	49050	24.0	
	HTCR-1	Room	40425	52450	15.5	
	HTCR-1	600	-	9100	60.5	
	HTSCR-1	Room	39900	52400	15.7	
	HTSCR-1	600	-	9900	60.5	
A6120 (4)	HST-1	Room	27250	50100	24.5	
Al-6% Mg	HST-1	600	-	11350	61.0	
0.49% Cr	HTCR-1	Room	42750	53550	14.5	
0.07% Ti	HTCR-1	600	-	10625	59.5	
	HTSCR-1	Room	41900	53200	14.0	
	HTSCR-1	600	-	10625	66.0	

*Heat Treatment - HT - solution heat-treated at 810-820 F for the time indicated by the number attached and quenched in cold water. An "S" following the HT indicates the alloy has also been stabilized at 650 F for 24 hours. An "H" indicates the alloy was aged 16 hours at 350 F. A "CR" indicates the alloy was also reduced 5% by cold rolling. The order of the symbols indicates the order in which the treatments were carried out.

TABLE III

TENSILE PROPERTIES OF 347 STAINLESS STEEL (1)

Test Temperature °F	0.2% Yield Strength psi	Ultimate Strength psi	Elongation % in 2 in.	Reduction in Area-%	Modulus of Elasticity 10^6 psi
Room	35000	85000	40.0	50	29
300	34000	74500	47.0	75	27.5
500	32000	69000	41.0	74	26.1
800	31800	75500	35	70.5	24.1

TABLE IV

TENSILE PROPERTIES OF ZIRCONIUM (1)

Material	Test Temperature °F	Ultimate Strength psi	Elongation % in 2 in.	Modulus of Elasticity 10^6 psi
Arc-melted	Room	27000 - 39000	40	13.8
Crystal bar	200	22000 - 33000	50	
	400	16000 - 25000	55	
	600	12000 - 19000	60	10.5
Arc-melted	Room	52000	25	
Bureau of Mines	200	43000	35	
	400	31000	45	
	600	21000	50	

TABLE V

TENSILE PROPERTIES OF SPONGE ZIRCONIUM-TIN ALLOYS (5)

Per cent Tin	Test Temperature °F	0.2% Yield Strength psi	Ultimate Strength psi	Elongation % in 2-in.	Reduction in Area-%
0	Room	35800	56400	24	33
	500	11500	27100	35	44
	930	6300	11100	67	56
2	Room	43600	61700	18	26
	500	19400	33000	24	45
	930	13600	20700	42	40
3	Room	51000	69400	24	31
	500	38700	50800	23	45
	930	18200	27100	32	47
4	Room	64300	81200	17	30
	500	36600	47000	24	38
	930	25100	34000	24	35
5	Room	71500	86000	16	31
	500	41100	53500	20	33
	930	-	37100	2	2

TABLE VI

TENSILE PROPERTIES OF ZIRCALOY-2 (6)

Heat Treatment	Test Temperature °F	0.2% Yield Strength psi	Ultimate Strength psi	Elongation % in 3 in.	Reduction in Area-%
standardized*	Room	70200	80300	12	20
	285	46000	55200	15	25
	320	43600	52400	16	23
	500	32100	39500	15	28
standardized without hydrogen solution treatment					
	500	29100	38500	16	18
vacuum annealed at 1850 F (1010 C)					
	500	26900	35200	22	23
standardized then hot rolled from 186 DPH to 215 DPH					
	500	37000	44600	10	23
vacuum annealed 20 hours at 1380 F (750 C) and hydrogen solution treated					
	Room	44700	69000	24	37
	300	28800	44900	37	51
	500	18300	31900	36	58
	600	16300	28700	38	51
	750	15900	26000	35	56
	900	10500	22100	36	50

* Held at 1850 F (1010 C) in helium 3/4 hour and water quenched machined specimens annealed at 1290 F (700 C) in vacuum less than 0.3 micron 1 hour and furnace cooled.

Hydrogen solution treatment 600 F (316 C) 3 hours and water quenched.

TABLE VII

NOTCH TENSILE TESTS OF ZIRCALOY-2 (7)

Heat Treatment	Test Temperature °F	Ultimate Strength psi	Elongation % in 3-in. gauge	Reduction in Area %
1*	unnotched - 320	137200	15	14
	notched - 320	202400	--	6
	unnotched Room	75000	16	32
	notched Room	140800	--	10
	unnotched 390	46500	24	50
	notched 390	99000	--	22
2*	unnotched - 320	127600	18	24
	notched - 320	190200	--	2
	unnotched Room	70400	19	40
	notched Room	127400	--	10
	unnotched 390	40000	28	56
	notched 390	74500	--	17

0.25 inch diameter specimens - notched 60°, 0.099-inches deep with root radius 0.01 inch. 3.5 theoretical stress concentration factor. Notched specimens 0.25-inch diameter at base of notch.

* Treatment 1 - heated 3/4 hour in helium at 1850 F (1010 C) and water quenched. Machined specimens annealed in vacuum 1 hour at 1290 F (700 C).

* Treatment 2 - rolled 5 per cent - specimens annealed in vacuum 20 hours at 1380 F (750 C) and furnace cooled.

Figure 1

ELEVATED TEMPERATURE YIELD STRENGTH OF SELECTED MATERIALS
Compiled from references (1,2,3,4,5,6)

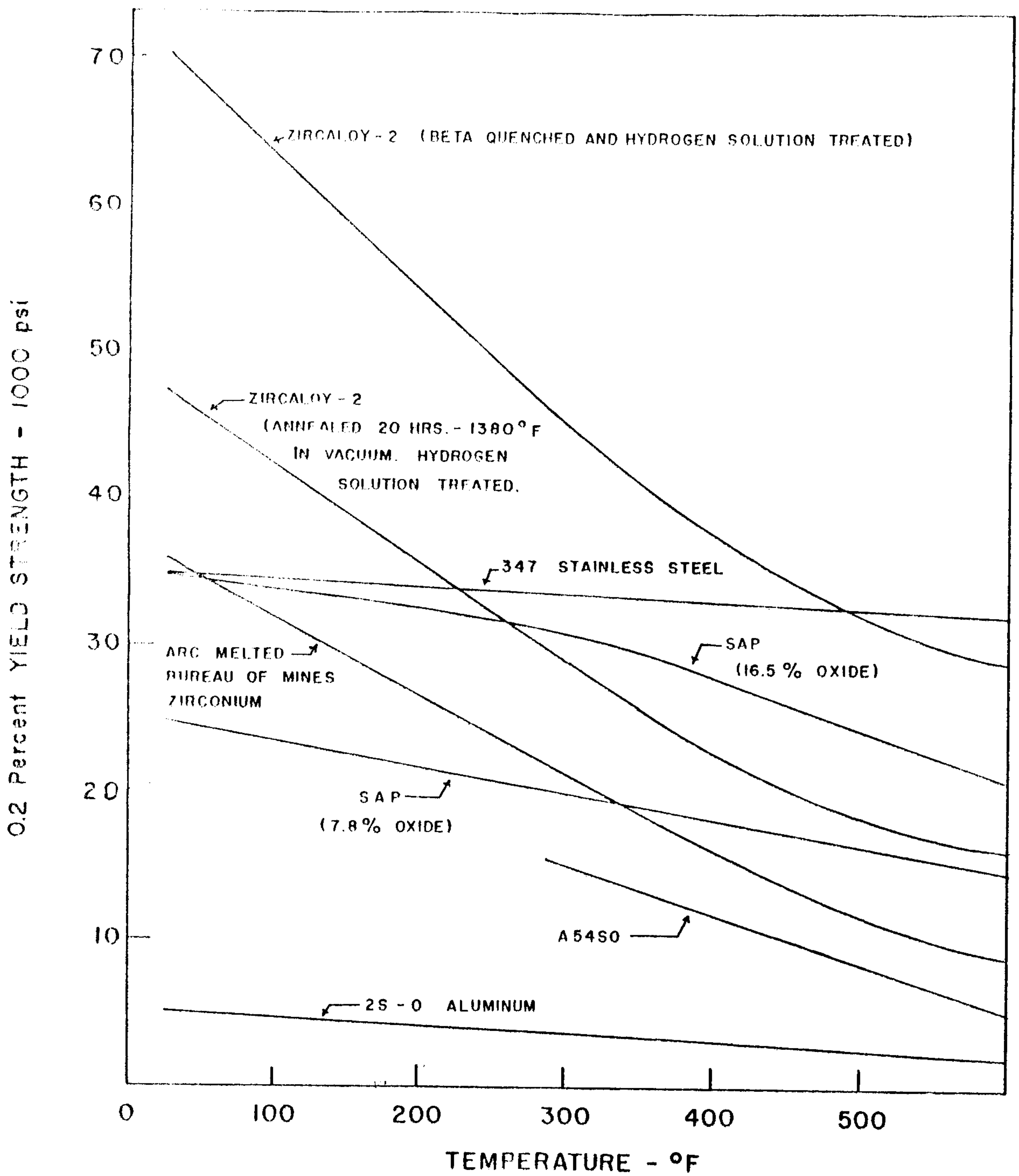
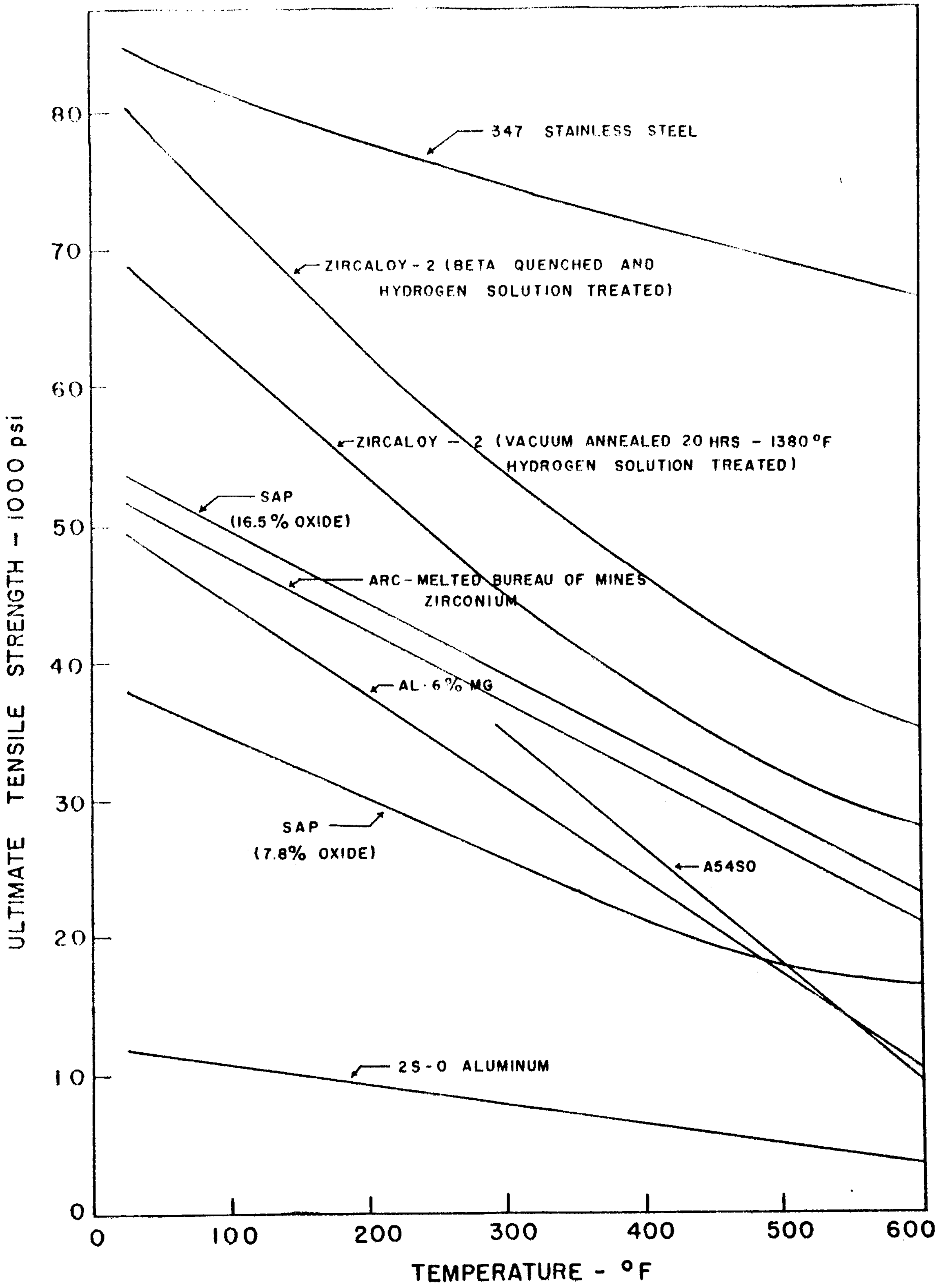


Figure 2

ELEVATED TEMPERATURE TENSILE STRENGTH OF SELECTED MATERIALS
Compiled from references (1,2,3,4,5,6)



Impact Properties

The impact strength of zirconium, zirconium-tin alloys and Zircaloy-2 are shown in Tables VIII, IX, and X. These measurements show a transition at about 390 F (200 C), with much higher impact strengths above this temperature than below it. Investigators at WAPD and BMI have determined that the low temperature ductility is improved considerably by heating at 600 F or higher and water quenching. On slow cooling from temperatures of 600 F or higher the impact strengths are low and this has been associated with the precipitation of zirconium hydride. Quenching from the solution temperature prevents precipitation of the hydride phase and the material is more ductile. Table XI illustrates the effect of hydrogen content on the impact strength. It is seen that very minute quantities of hydrogen can embrittle the material and, as indicated in Table XI, impair the impact strength at proposed operating temperatures.

Type 347 stainless steel retains its toughness at low temperatures with Charpy V-notch impact values of 31 ft-lb at 70 F to 36 ft-lb at 105 F.

No impact test data are available for the aluminum-aluminum oxide alloys although their impact strengths would be expected to be low based on the low ductility at elevated temperatures.

Fatigue Properties

Only scattered data are available on the fatigue properties of these materials. The endurance limit of Zircaloy-2 at 600 F in the beta treated condition is reported to be 27,000 psi for unnotched round samples and less than 12,000 psi when notched for 2.7 theoretical stress concentration factor.[9] The endurance limit of this material after annealing for 20 hours at 1380 F (750 C) and furnace cooling is 28,000 psi for unnotched samples and 9,000 psi for notched bars.[7]

The stress for a life of 2 x 10^6 cycles in tension-fatigue with the minimum stress zero for the 10-13 per cent Al_2O_3-aluminum alloy is 26,300 psi at room temperature and 17,100 psi at 600 F. In rotating beam tests the stress for a life of 10^8 cycles for this material is 15,000 psi at room temperature on unnotched bars and 10,700 psi on bars notched to obtain a 1.4 notch sensitivity factor.[2]

In cantilever beam fatigue tests the 7.8 per cent Al_2O_3-aluminum alloy can withstand 6,000-8,000 psi at 400-600 F for 10^8 cycles.[3]

Creep Properties

The limited creep data available for these materials in the temperature range 300-600 F do not permit the construction of complete design curves. The scattered results shown in Tables XII, XIII, XIV, XV, XVI, XVII, and XVIII are sufficient however to establish approximate limiting stresses for a creep rate not greater than 10^{-5} in/in/hr at 600 F.

The largest portion of the creep data shown for zirconium and the zirconium-tin alloys was obtained at 500 F. BMI has reported that at "stress levels approximating the short time tensile yield strength at 500 F, secondary creep rates for zirconium and zirconium-tin alloys are practically insignificant. Deformation of these alloys

TABLE VIII

V-NOTCH CHARPY TESTS OF ZIRCONIUM AND ZIRCONIUM-2-1/2% TIN ALLOY (8)

Material	Energy - ft-lbs - °F -100	0	200	300	400	500	600
arc-melted crystal bar	20	20	25	35	65	94	104
crystal bar-2-1/2% Sn	12	15	24	40	70	94	

TABLE IX

IMPACT PROPERTIES OF ZIRCONIUM-TIN ALLOYS (5)

Alloy Per cent Sn	Energy - ft-lbs - °F 72	212	392	482	572	662	752
0	12	20	30 44	36	32 42	44	60 46
2	17	--	33 19	34	39	45	48 41
3	13	--	20 16	33	42	45	44 32

Induction melted Bureau of Mines sponge-specimen annealed 1 hour at 1290 F (700 C). V-notch charpy test.

TABLE X

IMPACT PROPERTIES OF ZIRCALOY-2 (6)

Temperature °F	Energy - ft-lbs Beta Quenched* D27**	D30**	Beta Quenched aged 3 hrs. at 600 F, slow cool D27	D30
-320	6	6	4	4
32	16	13	6	6
212	34	26	7	7
390	72	55	14	13
570	104	103	110	95

* Heated at 1850 F (1010 C) in helium - water quenched
** D27 and D30 are separate zircaloy ingots

TABLE XI

EFFECT OF HYDROGEN CONTENT ON IMPACT STRENGTH (6)

Test Temperature °F	Impact Strength - ft-lb 3.3 ppm H_2	250 ppm H_2	500 ppm H_2
-320	16	2	2
-105	25	-	-
32	52	2	2
212	59	3	2
392	57	4	2
572	51	8	5

Heated at 600 F 3 hours and furnace cooled.

TABLE XII

CREEP PROPERTIES OF 347 STAINLESS STEEL (1)

	1000 F psi	1100 F psi	1300 F psi	1500 F psi
creep strength for a life of 10,000 hours with 1% elongation	20000	14000	5500	850

TABLE XIII

CREEP PROPERTIES OF SAP (3)

	0.5% Al_2O_3 300 F	400 F	7.8% Al_2O_3 500 F	600 F
stress to cause creep rate of				
0.000001 in/in/hr	9500			
0.00001 in/in/hr	10500	16000	13000	10500
0.0001 in/in/hr		17000	14000	11500
0.001 in/in/hr		17500	14500	12500
stress to cause failure in				
10 hours		18000	15000	12500
100 hours		17000	14000	11500
1000 hours		16000	13000	10500

TABLE XIV

CREEP TESTS OF AL-6% Mg ALLOY (4)

Alloy*	Heat* Treatment	Temperature °F	Stress psi	Duration hours	Initial Deformation %	Final Deformation %	Minimum Creep Rate %/hr
A5980	HTS-1	600	2000	289	0.050	0.117	0.00034
		600	2000	358	0.050	0.182	0.00020
A6120	HTS-1	600	2000	480	0.050	-	0.00010
		600	2000	340	0.050	0.106	0.00005

* Heat-treatment and composition as given in Table II.

TABLE XV

CREEP TESTS OF ZIRCONIUM AND ZIRCONIUM ALLOYS

Material	Temperature °F	Stress psi	Minimum Creep Rate 10^{-5}%/hr
crystal bar Zr (1)	500	14000	10
crystal bar Zr (1)	500	16000	37
crystal bar Zr (10)	500	10000	0.3
crystal bar Zr (10)	500	11500	300
zircaloy-2 (7)	650	24575	3.5
zircaloy-2 (7)	650	26500	9.5

TABLE XVI

CREEP TESTS OF ZIRCONIUM-TIN ALLOYS (11)

Temperature °F	Stress psi	Deformation in 100 hrs-%	Total Time hours	Total Deformation %	Approximate Minimum Creep Rate 10^{-5}%/hr
Arc-melted crystal bar - 2.5 per cent tin alloy					
500	26000	10.4	817	10.4	nil
500	23000	2.4	650	2.4	nil
500	21000	1.1	1350	1.4	nil
500	20000	0.25	2545	0.30	1
500	18000	0.22	1007	0.24	1
Bureau of Mines Zr - 2.8 per cent tin alloy					
500	27000	2.48	330	2.5	20
500	25000	0.43	1675	0.48	1

TABLE XVII

CREEP TUPTURE DATA ON ARC-MELTED CRYSTAL BAR ZIRCONIUM AT 500 F (260 C) (12)

Time to Rupture Hours	Stress - psi Longitudinal	Stress - psi Transverse
10	18000	14000
100	17000	14000
1000	16000	13000

TABLE XVIII

CREEP TESTS OF INDUCTION-MELTED BUREAU OF MINES TIN ALLOYS AT 500 F (260 C) (13)

Alloy % Sn	Stress at 500 F-psi	Deformation in 10 hours - %	Deformation in 1000 hours - %	Minimum Creep Rate 10^{-5}%/hr	Stress to Cause 1% Elongation in 1000 hrs
0	12000	0.57	0.64	4	14000
	10000	0.36	0.38	nil	
2	21000	0.95	--	2	
	20000	0.74	0.75	nil	
	18000	0.46	0.48	nil	
	16000	0.35	0.36	nil	21000
3	35000	3.4	--	6	
	30000	1.45	1.50(est)	2	
	27000	1.06	--	nil	
	24000	0.53	0.55	nil	26000

takes place almost entirely in the first 10 hours under such a stress."[13] Limited data shown for Zircaloy-2 at 650 F indicates that this observation applies also at higher temperatures.

The creep of the Al - 6 per cent Mg alloys is excessive at stresses of only 2,000 psi and for internal tube pressures of 1,500 psi. These alloys could not be considered.

Effect of Irradiation on Properties

The property changes occuring in structural materials due to neutron bombardment depend to a large extent on the temperature during exposure. Most of the changes are similar to those produced by cold working and are annealed out or healed at temperatures lower than those required for recovery of cold working effects.

In general, the changes observed are:

1. Increase in tensile and yield strength.
2. Creep rates of some metals are sometimes accelerated and sometimes retarded during irradiation depending on the stress and temperature.
3. Decrease in ductility.
4. Impact transition temperature for ductile to brittle fracture is raised.
5. Increase in electrical resistivity and decrease in thermal conductivity.
6. Increase in penetration hardness.

The results of specific tests on 347 stainless steel and zirconium are shown in Tables XIX, XX, and XXI. In many cases the tensile property measurements were made on sub-size specimens and are not directly comparable to tests made with standard size specimens.

For these materials slight increases in strength and decreases in ductility could be expected due to exposure to irradiation. The creep rates of both 347 stainless steel and zirconium are decreased during irradiation at temperatures and stress levels comparable to the expected operating conditions.[18, 19, 20]

Changes in thermal conductivity due to neutron bombardment at these temperatures would be expected to be negligible on the basis of electrical resistivity measurements.[7]

Comparison of Materials

Both sponge zirconium and Zircaloy-2 have satisfactory mechanical and physical properties for use as tubes and jackets under the conditions of temperature and pressure assumed for the dual purpose reactor. The thermal conductivity is not comparable to that of aluminum but is as good as stainless steel. The coefficient of thermal expansion is less than half that of either steel or aluminum. This could prove advantageous since it is also less than uranium and should insure a tight bond between jacket and slug. Zircaloy-2 is definitely superior to sponge zirconium in high temperature tensile properties. Only stainless of the materials considered is comparable to Zircaloy-2 insofar as tensile strength at elevated temperatures is considered. Zirconium and Zircaloy-2 have adequate creep and fatigue properties, based on the somewhat limited data. Impact strengths at room temperature are

TABLE XIX

IRRADIATION EFFECTS ON THE TENSILE PROPERTIES OF 347 STAINLESS STEEL

Condition	Specimen Gauge inches	Total Flux 10^{19} nvt slow	Total Flux 10^{19} nvt fast	0.2% Yield Strength 1000 psi control	0.2% Yield Strength 1000 psi irradiated	Ultimate Strength 1000 psi control	Ultimate Strength 1000 psi irradiated	Elongation Per cent control	Elongation Per cent irradiated
annealed	1/32 x 1-1/2	2	0.7†	-	-	82.0	112.5	16	16
sheet	0.075 x 0.075 x 1	22	30 I	32.5	76.9	85.6	102.8	55	34
sheet	0.075 x 0.075 x 1	36	50 I	32.5	86.3	85.6	107.0	55	29
sheet	0.020 x 0.25 x 1	22	30 I	32.9	81.5	86.3	105.8	62	37
sheet	0.020 x 0.25 x 1	36	50 I	32.9	74.5	86.3	103.7	62	37
			25*	59.7	68.2	95.7	99.7		

† Hanford test hole (ANL DATA)

I Hanford hollow uranium slugs (14)

* Chalk River at 500 F (7)

Condition	0.2% Yield Strength psi	Ultimate Strength psi	Uniform Elongation Per cent	Elongation to Fracture 4 x diam. gauge Per cent
unirradiated	47500	98100	41.6	54.1
	51600	95400	45.4	54.1
irradiated*	78200	104500	35.9	46.0
	76500	104100	36.3	--

* Hanford Reactor, 6 - 8 x 10^{19} nvt (thermal) at > 50 C (15)

TABLE XX

EFFECT OF IRRADIATION UPON BRINELL HARDNESS OF SHEET SS-347 FOR VARIOUS DEGREES OF COLD WORK(16)

Reduction in Thickness Per cent	Initial Hardness	Hardness After Indicated Thermal nvt 6.3×10^{19}	1.5×10^{20}	2.3×10^{20}
0	143	216	223	227
10	223	259	273	290
19.8	265	291	298	300
32.5	302	327	339	343
38.8	319	343	348	352
50.2	328	356	359	369

TABLE XXI

IRRADIATION EFFECTS ON THE TENSILE PROPERTIES OF ZIRCONIUM

Material	Total Flux 10^{19} nvt slow	fast	0.2% Yield Strength psi control	irradiated	Ultimate Strength psi control	irradiated	Elongation Per cent control	irradiated
crystal bar Zr		25*	15000	22700	39000	38500	-	-
---	4.8†		56000	64000	64000	69500	14	12

* Chalk River at 500 F (7)

† Brookhaven at 270 F (17)

satisfactory, providing the zirconium has not picked up excessive hydrogen. Insufficient data are available to permit evaluation of the importance of the loss in impact strength due to the hydrogen embrittlement.

Aluminum and its alloys, including SAP, have superior thermal conductivity and satisfactory coefficients of thermal expansion. Only SAP has adequate high temperature mechanical properties due to the excessive creep rates of the various aluminum alloys. SAP has good high temperature tensile properties, but the ductility decreases with increasing temperature. Both fatigue and creep properties of SAP are satisfactory. Nothing is known of the impact properties, but they are presumed to be low based on the low ductility.

Stainless steel has an adequate thermal conductivity and coefficient of thermal expansion. Its mechanical properties at elevated temperatures are excellent. The high temperature tensile and creep properties are excellent, and the low temperature impact strengths are satisfactory.

Based on the physical and mechanical properties above, all of the materials are satisfactory for jackets, and SAP, 347 stainless steel, zirconium, and Zircaloy-2 should have adequate high temperature mechanical properties to insure a long tube life under the conditions of temperature and pressure considered.

Corrosion

Two types of corrosion must be considered in the pile. The first, common to both tubes and jackets, is high temperature aqueous corrosion. This corrosion may be complicated somewhat by special types such as weld, intergranular, or stress corrosion, but these are merely facets of the overall corrosion problem. The second type of corrosion is believed to be primarily an oxidation problem between the outer surfaces of the tubes and the pile atmosphere. This atmosphere at temperatures in excess of 500 C (850 F) should consist in large part of helium, but there may be carbon dioxide and such impurities as oxygen, hydrogen, and water vapor present; therefore, the possibilities of reaction or attack by such an atmosphere, plus the irradiation effect on this oxidation rate, must be considered.

Zirconium

Aqueous corrosion does not appear to be a problem with Zircaloy-2 within the range 200-300 C, and the same is true for sponge zirconium if carbon and nitrogen contents are controlled adequately. Extensive programs are being carried out at the Bureau of Mines, MIT, and Westinghouse to determine the aqueous corrosion resistance of zirconium and its alloys, and the data now available indicate that corrosion can be readily or inexpensively controlled by controlling the chemical composition. Work at MIT has indicated that carbon pickup drastically decreases the corrosion resistance of unalloyed zirconium.[21] Overall corrosion resistance drops at 600 F (315 C), and localized attack occurs at the carbide particles in water at temperatures as low as 250 F (120 C). Alloying with 1-2.5 per cent tin permits carbon contents as great as 0.15 per cent. Zircaloy-2, which contains 1.5 per cent tin, has proven adequate to 680 F (360 C) in water or 750 F (400 C) in steam for short periods of time. The time appears to be a function of impurity content. There is some question whether the Zircaloys retain their corrosion resistance at these temperatures. It is suspected that Zircaloy-2 may eventually corrode at an accelerated rate similar to

the rates observed with arc melted zirconium-tin alloys.(21) Further work now in progress does not confirm this accelerated corrosion.(22)

Bureau of Mines sponge zirconium has satisfactory corrosion resistance at 600 F (315 C) in water if carbon and nitrogen are controlled with carbon held to 120 and nitrogen to 24 ppm. An average weight gain of only 0.16 mg/cm^2 was observed at this temperature after 1200 hours.(23) Two 18 hour periods at 750 F (400 C) in 1500 psi steam did not cause excessive corrosion. Results were comparable to crystal bar zirconium, indicating that the differences in corrosion resistance observed between sponge and crystal bar zirconium are due to impurities rather than to the methods of production.

Considerable work has been done on Zircaloy-2 at the Bureau of Mines. Variability was observed in Zircaloy-2 with some specimens displaying abnormal weight gains after 14 days in 600 F (315 C) water,(24) while others were satisfactory at this and higher temperatures for longer times.(25) Zircaloy-2 gained 15 mg/dm^2 in 56 days at 600 F (315 C). The gain in 750 F (460 C) steam was 48 mg/dm^2 in 48 days. This compares to gains of 100 mg/dm^2 in 140 days at 600 F (315 C) for unalloyed zirconium. The control of the nitrogen content is important in both unalloyed and alloyed zirconium. A pronounced decrease in corrosion resistance occurs with an increase in the nitrogen content.(26) There is some evidence that a limiting nitrogen content exists, which tends to contradict the preceding statement regarding nitrogen. Work at BMI indicates that nitrogen in the range 40-360 parts per million has no effect on the corrosion rate of Zircaloy-2.(27) This should be confirmed by additional work.

One desirable aspect of zirconium is the fact that cold working up to 50 per cent has little or no effect on the corrosion rates.(24,25) If the samples are cold worked more extensively, annealing is necessary because complete breakdown due to corrosion at 600 F (315 C) has been observed in zirconium in 56 days. Additional data are required to see if Zircaloy-2 behaves similarly. This factor is of particular interest in tube fabrication since cold reductions in the vicinity of 65 per cent have been considered.

It is apparent on examining the preceding statements that there is some contradiction concerning the behavior of zirconium or Zircaloy-2 in aqueous media at temperatures of 600 F or higher. The most important problem would appear to be the long time corrosion resistance of Zircaloy-2. Results appear to be favorable, but tests at longer times must be conducted before this problem is settled. Additional data are also necessary to determine if irradiation has a deleterious effect on the corrosion rate in aqueous media.

The corrosion of zirconium and its alloys, when exposed to in-pile atmospheres, may well be the factor limiting the use of zirconium in a reactor. Results now available are somewhat limited, but the rates of attack are excessive. Zirconium, when exposed to air, forms two oxides. The first is adherent, but this is soon converted to the second which spalls severely. Before conversion the corrosion mechanism appears to be parabolic, but after conversion it is approximately linear. At 1100 F (595 C) the rate is about 300 mg/dm^2/day. At 1200 F (650 C) it has increased to about 750 mg/dm^2/day;(28) and at 1300 F (705 C) the rate is 2500 mg/dm^2/day.(28) When one realizes that the penetration rate at 1100 F (595 C) corresponds to about 0.1 inches per year, the seriousness of the problem is apparent. Anticipated operating conditions should result in lower corrosion rates since the

metal and gas temperatures will be much lower.

Four factors must be evaluated before it is known how much of a problem this oxidation is. The effect of alloying must be considered since the most favorable material for tubes is believed to be Zircaloy-2. Previous work indicates that aluminum, at least, when alloyed with zirconium decreases the resistance to oxidation.[28] There is a definite possibility that the tin in Zircaloy-2 will have a similar effect so it is essential that this factor be evaluated as soon as possible. The second factor is the effect of irradiation on the oxidation rate of zirconium. Here again there appears to be no reason to believe that irradiation will affect the rate to a marked degree, but this must be determined experimentally. A third factor is the effect of composition of atmosphere on the corrosion rate. Some work indicates that an increase in oxygen in the atmosphere is accompanied by an increase in the oxidation rate.[28] Other work indicates there is little or no change in the rate of reaction with a change in the oxygen content.[29] This is extremely important since it may be possible that helium atmospheres with nominal contents of oxygen, hydrogen, and water vapor do not promote excessive oxidation. If very pure helium is required, together with extensive control against atmospheric leakage into the pile, the capital investment may be markedly increased. The fourth factor is the temperature differential between metal and gas. Oxidation tests represent an equilibrium condition between the atmosphere and the specimen. The oxidation rate is that occurring for the metal at this temperature with the gas at the same temperature. In the pile the tubes, due to the water inside, have an outside temperature much less than that of the pile atmosphere. It is assumed that this condition should result in lower oxidation rates, but some work must be done to verify this and to determine the degree of change in rate that results.

The high oxidation rates of zirconium in air may be the limiting factor in the use of this material. Suitable in-pile tests should be conducted to determine the effect of metal composition, atmosphere, irradiation, and thermal gradient on zirconium and its alloys. Thermal gradient refers to the temperature differential between metal surface and gas. Alternate possibilities consist of cladding or coating the exterior of the tubes to minimize the attack.

Stainless Steel

Neither aqueous corrosion nor oxidation appears to be a factor limiting the use of stainless steel or low alloy steel as jackets or tubes. Both materials have been used in high pressure boilers. With stainless steel no precautions need be taken if the water is relatively pure. Chloride ion is undesirable, but this is not a factor in boiler feed water and dissolved oxygen is actually advantageous in improving the corrosion resistance. Low alloy steel has been used in boilers for many years; the only precautions are some pH control and deaeration of the water to minimize scale formation. The effects of irradiation are not completely known, but the KAPL-120 (ANL-140) high temperature loop in H pile has operated satisfactorily for 4 years. An adherent black deposit built up on the internal surface of the stainless steel tube, but this did not appear to be disadvantageous. Tentatively the material has been identified as an oxide of iron resulting from the iron in the water or from some solution into the water. Since it does not appear to affect the heat transfer to a marked degree, its presence seems to be unimportant.

The atmosphere on the external side of the tube should not be a limiting factor

either. Nothing in this atmosphere as such would seem to cause sensitization or to promote corrosion unduly. Scaling does not begin with stainless steels below about 1500 F (815 C), well beyond the anticipated operating limits of the pile. With ordinary steels, scaling begins at about 1000 F (540 C).[30] There is no indication that pile conditions wil unduly affect the oxidation rates, so corrosion is not believed to be a limiting factor in the selection of stainless or low alloy steel for use as an in-pile material.

Aluminum

Aluminum alloys other than SAP do not appear to have the strength necessary for tubes; therefore, their oxidation due to the pile atmosphere is of little more than academic interest. It is possible that the aluminum-magnesium alloys may be borderline cases where their strengths are barely adequate over long periods of time. Unfortunately, aluminum alloys containing magnesium suffer from intergranular oxidation so there is a definite danger in using them when under stress.

SAP has desirable mechanical properties, but nothing is known of its resistance to oxidation at high temperatures. Since each particle is coated with oxide, it is presumed to be good, but this should be confirmed. No data are available on the high temperature aqueous corrosion of SAP so it is not possible to evaluate the material on this basis. This is of sufficient importance so that it is believed desirable to determine these data.

Although aluminum does not appear to be satisfactory as a tube material with the exception of SAP, there is a definite possibility that it would prove satisfactory as a jacket material. The work of Draley in the temperature range 395-570 F (200-300 C) indicates that 2S aluminum is feasible in high purity distilled water when pH control is used.[31] Pure aluminum is definitely unsatisfactory, but 2S or other alloys with sufficient silicon to prevent intergranular corrosion, do not corrode at excessive rates. Such effects as galvanic coupling, oxidants in the water, stressing of the specimens, or creep do not influence the corrosion rate in high purity water. Above 390 F (200 C) pH control is required due to the initiation of intergranular corrosion. By lowering the pH to 3.5 at 390 F (200 C) the corrosion rate is limited to 0.90 $mg/dm^2/day$ or to a penetration of 0.033 mils/month. This same pH is sufficient to protect the aluminum to temperatures at least as high as 480 F (250 C).

In the high purity water, radiation effects lead to an increase in the oxygen content which actually reduces the corrosion rate. This is the opposite of the results obtained in Hanford water and is attributed to absence of impurities.

An important factor which requires further evaluation is the apparent reduction in corrosion occurring when zirconium and aluminum are coupled. Conditions which lead to the disintegration of aluminum, i.e., high temperatures and high pH, are neutralized when these materials are coupled. When coupled with zirconium little or no attack on the aluminum is observed. This is particularly important, if it is true, because it might mean that no pH control would be required in a system consisting of aluminum jacketed slugs and zirconium tubes. The aluminum would minimize the corrosion of the zirconium while forming a tough adherent oxide film, and it might minimize corrosion where the zirconium is coupled to the stainless steel. Some work should be done to confirm this since it could result in a pronounced saving in 100, 200, and 300 Area costs.

One difficulty occurring in the case when aluminum is used for tubes and for jackets is the effect of the low pH on the materials outside the pile. Draley's work has indicated that it isn't the aluminum that fails at low pH and high temperatures; it is the stainless steel. If the aluminum tubes were coupled to stainless steel, it is quite possible that the interior of the steel would have to be clad. This would also be true for pumps and heat exchangers. The alternatives are aluminum tubes outside the pile, which is eliminated as a possibility because of insufficient strength, or special alloys such as the Inconels which would have adequate high temperature corrosion resistance. Such materials could be used for pipes, pumps, and other equipment, but this would result in a definite increase in capital investment due to their high costs.

Neutron Economy

An important factor in the selection of satisfactory tubes and jackets is the thermal utilization of the structural materials considered. A material may have superior mechanical and physical properties, but the macroscopic thermal neutron absorption cross section may be so high that all advantages accruing from the mechanical and physical properties and material cost are lost because of the excessive enrichment required.

The macroscopic cross sections for 1020 steel, 347 stainless steel, 2S aluminum, SAP (7.8 weight per cent oxide), a magnesium-aluminum alloy containing titanium and chromium, zirconium with 0, 100, and 200 ppm of hafnium, and Zircaloy-2 with 0, 100 and 200 ppm of hafnium have been determined. These values are shown in Table XXII, and it is obvious that the cross sections are grouped according to the principal constituent. Zirconium or Zircaloy-2 have cross sections of about 0.008, aluminum of 0.012, and the steels about 0.20. Thus, there is a fifty per cent increase in macroscopic section in the case of aluminum and a twenty-five fold increase in the case of steel when compared to zirconium. The factor in the case of steel is sufficient to minimize any advantages accruing from the superior mechanical properties.

The thermal utilizations for five tube-jacket combinations were evaluated to determine how satisfactory these materials were from the neutron economy standpoint. Conditions considered were a Zircaloy-2 tube with Zircaloy-2 jackets, 2S aluminum jackets or stainless steel jackets; aluminum (SAP) tubes and aluminum jackets; and stainless steel tubes and jackets. These combinations are believed to be those with some degree of feasibility. Tube wall thicknesses were determined on the basis of the high temperature creep and tensile properties. A safety factor of two was used with the yield strength selected as the limiting property. In the case of zirconium the tube wall thickness was doubled due to potential oxidation. Thicknesses of 0.1-inch for stainless steel and 0.2-inch for Zircaloy-2 and SAP were selected. Jacket thicknesses were established arbitrarily, assuming some decrease due to advantageous aqueous corrosion resistance and mechanical properties. Stainless steel was set at 0.015-inch, Zircaloy-2 at 0.030-inch, and aluminum at 0.050-inch.

The thermal utilization, f, was evaluated from the following equation:

$$\frac{1}{f} = \left(\frac{\Sigma_g V_g}{\Sigma_u V_u} + \frac{\Sigma_{H_2O} V_{H_2O}}{\Sigma_u V_u} + \frac{\Sigma_{tube} V_{tube}}{\Sigma_u V_u} + \frac{\Sigma_{jacket} V_{jacket}}{\Sigma_u V_u}\right) F + E - (E-1)\frac{q_{H_2O} V_{H_2O}}{q_g V_g + q_{H_2O}} + \left(\frac{\Sigma_g V_g}{V_u \Sigma_{H_2O}} \cdot \frac{K_{H_2O} V_0 k_{H_2O} t}{2}\right)$$

TABLE XXII

MACROSCOPIC CROSS SECTIONS OF VARIOUS STRUCTURAL METALS AND ALLOYS

Material	Σ cm^{-1}
1020 Steel	0.20
347 Stainless Steel	0.23
SAP (sintered aluminum powder) 7.8% oxide	0.010
Al plus 6% Mg, 0.5% Cr, 0.1% Ti	0.012
2S Aluminum	0.012
Zirconium	0.0077
Zirconium plus 100 ppm Hafnium	0.0080
Zirconium plus 200 ppm Hafnium	0.0083
Zircaloy-2	0.0082
Zircaloy-2 plus 100 ppm Hafnium	0.0084
Zircaloy-2 plus 200 ppm Hafnium	0.0087

TABLE XXIII

THERMAL UTILIZATION VALUES OF VARIOUS STRUCTURAL MATERIALS

Tube	Thickness	Jacket	Thickness	f = Thermal Utilization
Aluminum	0.20 in.	Aluminum	0.050	0.880
Zircaloy-2	0.20 in.	Zircaloy-2	0.030	0.891
Zircaloy-2	0.20 in.	Aluminum	0.030	0.889
Zircaloy-2	0.20 in.	347 SS	0.015	0.842
347 SS	0.10 in.	347 SS	0.015	0.696

The factors are listed in Appendix II, together with the accepted values used with a K pile lattice. It is realized that these may not represent the best values for a high temperature dual purpose reactor, but they do permit a comparison of the various structural materials.

A comparison of the thermal utilizations in Table XXIII indicates that the most satisfactory combination consists of Zircaloy-2 tubes and jackets, but aluminum jackets can be substituted for Zircaloy-2, or aluminum tubes and jackets can be used with only a slight loss in reactivity. A thin stainless steel jacket causes a definite decrease in thermal utilization and a stainless steel tube would necessitate a great deal of enrichment. The cost of these materials in terms of actual material cost plus enrichment cost will be dealt with in the 700 Area section since it is a matter of economics.

On the basis of the thermal utilization data alone there seems to be no reason for considering the steels since they are not competitive with Zircaloy-2 tubes and jackets or aluminum jackets. A limiting factor might prove to be aqueous corrosion which, if it eliminates aluminum, might make the steels appear more favorable.

The Zircaloy-2 combination of tubes and jackets is actually more favorable than is the case for the present lattice, based on these somewhat crude calculations. The thermal utilization is higher than is true for 2S aluminum tubes and jackets in the existing piles.

200 AREA

Problems in the 200 Area are primarily chemical and economic. A satisfactory method of dissolving the fuel from the jacket should exist; or if the jacket is also dissolved, it should not interfere with the recovery of plutonium and uranium. Finally, if it is necessary to recover the jacket material due to its cost, there should be adequate storage during the activity decay period and a satisfactory procedure for recovering the material in case of chemical solution. Obviously, recovery is only worthwhile in the case of zirconium or its alloys.

Zirconium

Due to its cost per pound there is a definite possibility that the jacket of zirconium or Zircaloy-2 will have to be recovered if the operation of the pile is to be profitable. The construction of some form of cracker to break the jacket so that the uranium can be selectively dissolved seems to be possible, but the expense of the equipment might well be excessive due to the high radiation levels requiring automatic handling so as not to expose the operators. Zirconium, if dissolved with the fuel, may prove to be a problem in product extraction, but this is not believed to be the case, provided that recovery of the zirconium is not necessary.[32] A third possibility is the selective dissolution of the zirconium jacket in a solvent which does not attack the fuel element.

Any recovery process will probably be quite expensive, and an extensive inventory will exist due to the slow decay of the 65 day Zr-95. This will mean that a period of about five years will elapse before the zirconium can be refabricated.

Aluminum

This will be the same as the existing case so no additional problems will occur.

Stainless Steel

It is assumed that no attempt to recover the steel will be made so the choice of a method will depend on the ease of removing the fuel from a stainless steel jacket or the lack of interference of the jacket in other stages if dissolved. Cracking the jacket will pose the same problems that would occur with zirconium. Dissolution of the jacket would require new equipment since the vessels now used are stainless steel. The only alloys for such vessels would be of the Inconel type which would be very expensive. Another difficulty would be the high activity induced during irradiation of these jackets, especially the long-lived activities.

300 AREA

Problems of concern in the 300 Area are: the fabrication and flanging of tubes; their connection to the piping on the external face; the jacketing of slugs; and the heat treatment of slugs prior to insertion in the pile. Heat treatment is a factor in that it might sensitize the jacket material, promoting corrosion.

Zirconium

The fabrication of tubes does not appear to be a problem. Satisfactory results have been obtained in fabricating seamless tubes from both crystal bar and sponge zirconium and Zircaloy-1 so it may be assumed that Zircaloy-2 would present no difficulties. The most satisfactory method consists of coating with copper to prevent galling, hot extrusion to form the tube ribs, and a cold drawing to reduce the wall thickness and obtain the proper tube length. The copper can be removed by pickling. Results have been satisfactory with a 60 per cent reduction on cold drawing, and no difficulty is visualized in increasing the reduction to 65 per cent. This would be advantageous because the present tube draw benches are not long enough to take a tube extruded for a 60 per cent reduction, but are long enough for 65 per cent. Equipment for the 65 per cent cold draw is available, and adapting the present machines or purchasing new ones would be expensive. One factor must be considered before deciding that a 65 per cent reduction is most favorable; that is the corrosion of the alloy. Zirconium displays no pronounced change in corrosion resistance with less than 50 per cent cold work, but fails rapidly at higher percentages. An alternative would be an anneal at some intermediate stage, or following reduction. The last is undesirable since this would reduce the mechanical properties markedly. Some work needs to be done to determine the influence of cold work in various degrees on the corrosion rates of Zircaloy-2 in the temperature range of interest. This will probably determine the method of producing the tubes.

The method of tube fabrication outlined above is the most satisfactory since it is adaptable to zirconium or zirconium alloys, it gives markedly superior mechanical properties, the ribs are of uniform thickness, and there is a uniform grain size. An alternative method has been developed where the zirconium is rolled into a sheet; the ribs are then roll formed; the sheet is formed into a tube and closure is made by a weld. There are several disadvantages to this method. Welding produces a coarse grain and the soft annealed sheet has poor mechanical properties, the roll

formed ribs are thin, being no thicker than the wall, and the process is limited to crystal bar zirconium because sponge zirconium has sufficient gas in it to lower the surface ductility to the point where ribs cannot be roll formed. This method has been developed, but the disadvantages are so pronounced that it is not believed worthy of consideration.[33]

One difficulty which has not been discussed may be of considerable importance. Zirconium picks up hydrogen, and this hydrogen pickup results in a marked reduction in ductility and impact properties. Therefore, the effect of pickling on the properties should be evaluated to determine if it has caused an excessive drop in impact strength. This is also of importance in the jacket since there are many operations which could promote hydrogen pickup. It is possible that this sharply reduced ductility, when coupled with the negative coefficient of thermal expansion of zirconium compared to uranium, could cause side splits. Insufficient data are now available to determine if this is a significant factor.

The problem of jacketing uranium with zirconium is not solved, at this time, and, depending on the specifications established, may continue to be a source of difficulty. Four jacketing possibilities appear logical: a diffusion bond between the uranium and the zirconium; a dip method using a layer of some other metal to form the bond between the uranium and the zirconium; a press fit where heat transfer depends on the tight contact between the uranium and zirconium which is promoted by the sizing of the jacket on the slug and the differential of thermal expansion coefficients; casting the uranium into a zirconium sleeve.

Diffusion bonding has been attempted by co-extrusion, hot rolling, and hot pressing. Both co-extrusion and hot rolling form such a diffusion bond but extensive reductions in cross section are required to develop the bond. Unfortunately the bond is extremely friable and any shock usually results in it fracturing.[34] The shear strength of a diffusion bond between uranium and zirconium has been quoted as about 6000 psi,[35] but this results from a long-time high temperature diffusion, which probably gives a much stronger bond than that formed by hot rolling. Another difficulty in this method is the lack of a bond between the slug and the cap. Hot pressing has not formed a satisfactory bond to the present; alternate possibilities are higher temperatures and longer times, but there is a definite economic balance in such an operation. Another possibility is the insertion of an insulator between cap and slug, foregoing any bond. This has been done with some degree of success. Before the hot pressing or insertion of an insulator the hot rolled or co-extruded rod must be cut into the proper lengths and some uranium machined out at the ends to permit the insertion of the end caps. This machining is an expensive operation and can lead to considerable scrap unless definite precautions are taken. Closure by Heliarc welding is relatively simple and no difficulties are said to be experienced with such welds.

An examination of the operations in the preceding method of jacketing indicate that the rolling, sectioning, and machining operations would be expensive; there is no assurance that a permanent bond is formed on the sides; and there is no bonding at the ends.

An alternative method is the deep drawing of cans and a canning procedure comparable to the one now in use. Little or no work has been done on such a method so its feasibility cannot be evaluated. AlSi has been suggested for such a bond and other

materials are probably feasible. If a secondary barrier is desired this method may have some application.

A third method consists of inserting a slug into a deep drawn can and hot pressing the slug into the can or cold sizing the can onto the slug to promote intimate contact between the uranium and the zirconium. The cold sizing operation appears to be the cheapest and easiest. The final step would consist of welding on the cap which was inserted prior to cold sizing. On heating such a jacketed slug the lower coefficient of thermal expansion of zirconium should promote a more intimate contact between slug and jacket. The only possible effect that could result from this stressing would appear to be relaxation which would not reduce the intimacy of the bond. This method suffers from two potential disadvantages. The first is the heat transfer at the metal-metal interface; the second is the lack of a secondary barrier in case of jacket rupture or leakage. The heat transfer could be evaluated without too much difficulty, and the second factor is a function of the integrity of the jacket and the methods of inspection. It is also possible to plate or vapor deposit a sweater before jacketing in this fashion. The advantages of such a method, provided that heat transfer is no problem are obvious. It is simple, rapid, and much less expensive than the alternate methods.[34]

One other method of jacketing would be to cast the uranium directly into a zirconium jacket, and cap after homogenization or reduction. There are insufficient data now available to permit an evaluation of this method.

Aluminum

The only aluminum base material having potentialities as a high temperature, high pressure tube material is believed to be SAP. Extrusion of tubes is possible providing the oxide content is limited to less than 8 per cent, based on present data. The Van Stoning of the tubes may prove to be quite a problem, and alternate methods of making contact between the tubes and the external piping are difficult due to the impossibility of welding, brazing, or soldering SAP.

The canning of slugs in aluminum is not discussed here since it is the method now used, and presents no major difficulties.

Stainless Steel

Nothing is known of the jacketing of slugs in stainless steel. No difficulties are visualized in closure by welding or in cold drawing a jacket on a slug. A barrier such as silver will probably be required to prevent interdiffusion of uranium and steel, forming a low melting point eutectic.

Stainless steel tubes are believed to be eliminated on the basis of neutron economy. If not, there should be no fabrication problems with this material since the cross section of the tube is relatively simple.

700 AREA

Problems limited to the 700 Area would appear to be those of design and economics. Since the dimensions of the tubes are essentially the same, no design problem is believed to exist for one material as contrasted to another. The second factor,

economics, will differ markedly. An economic balance must consider availability and cost, potential recovery of jacket material, and degree of enrichment required to compensate for lost reactivity when materials with high capture cross sections are used.

Tubes

The only problem in the case of tubes is the initial capital investment and life in the pile. The life in the pile will probably be controlled by the aqueous and gaseous corrosion, and insufficient data are available to evaluate these factors completely. In the case of stainless steel the life of the tubes should be amortized over the life of the pile. In the case of SAP the information is much too limited to permit an estimate of the tube life. Nothing is known about the cost of SAP, but it is safe to assume that it is greater than any aluminum alloy, but substantially less than zirconium. The cost of zirconium can be set at about twenty dollars per pound, based on an extrapolation of present cost data. A factor which must be evaluated is the oxidation rate in the pile since it will determine the wall thickness and tube life.

The economic analysis which will follow the next section is approximate due to unavailability of accurate cost data and the inability to evaluate the factors affecting tube life, due to insufficient data.

Jackets

The problem in jackets is one of material cost in the fabricated form, canning costs, loss of reactivity in the pile due to the jacket, and recovery value if recovery is attempted.

PROBLEMS AND SUGGESTED FUTURE WORK

There are still insufficient data to permit a complete evaluation of zirconium or the other candidate materials. This section lists the major problems and suggests possible methods of attack.

Zirconium

(1) The in-pile oxidation due to the pile atmosphere. There are insufficient data available at present to determine the effect of this factor. The influence of alloying, irradiation, atmosphere composition, and differential sample-atmosphere temperature should be studied. This is believed to be the most important problem and may limit the use of zirconium.

(2) The cladding or coating of tubes. If oxidation limits the use of zirconium for tubes, work should be conducted to evaluate coatings for the exterior of the tubes to act as an atmosphere barrier. This work should parallel the oxidation studies.

(3) The in-pile aqueous corrosion of zirconium and Zircaloy-2. Existing information is good on the aqueous corrosion of zirconium out-of-pile, but some in-pile tests should be conducted with particular emphasis on the effect of cold work in percentages greater than 50 on the corrosion rates in the temperature range 200-300 C. The long time corrosion resistance of Zircaloy-2 should be determined.

(4) Jacketing. Extensive work is required here, including in-pile tests. It is suggested that cold sized slugs be tested to determine if the heat transfer is satisfactory, and if the jackets are free from defects. Additional work is required on other canning methods such as diffusion bonding, dip canning, and casting.

(5) Jacket recovery. The 200 Area problems should be evaluated and an economic balance conducted to determine the recovery cost versus the value of the recovered product.

(6) Hydrogen embrittlement of zirconium. The effect of hydrogen on the impact properties and ductility of zirconium and Zircaloy-2 should be determined. The amount of hydrogen pickup in pickling, heat-treatment, canning, or operation in the pile should be determined to see if this is a limiting factor in the use of zirconium tubes and jackets.

Aluminum

(7) Properties of SAP. If technically acceptable, this material would be economically attractive relative to zirconium. Extensive work is required to determine the high temperature mechanical and physical properties, corrosion and oxidation resistance, influence of irradiation, and fabricability of this material.

(8) Aqueous Corrosion of Aluminum. The use of 2S aluminum jackets would represent a large saving. The only factor limiting the use of 2S is believed to be the corrosion rate. Some high temperature tests should be conducted to determine the effect

of water quality on corrosion rates and particular emphasis should be placed on zirconium-aluminum couples to determine if this coupling enhances the corrosion resistance. Such a study based on Draley's work, could be quite readily achieved. As an adjunct to this study some alternate aluminum alloys should be checked for use in the existing reactors, particularly as tube materials since higher temperatures and pressures may result in excessive creep of the 2S tubes. Some of the aluminum-magnesium alloys should be examined for this purpose.

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36. Chemical Engineering Process Equipment Costs

APPENDIX I

Approximate Tube Sizes Based on Mechanical Properties

The cost and neutron economy factors for these materials cannot be adequately compared without fixing approximate tube sizes. Several assumptions need to be made in order to make these calculations and these are discussed.

1. The operating conditions were assumed to be 600 F and internal tube pressures of 1500 psi.

2. These calculations were made neglecting the effects of corrosion.

3. The inner radius of the tube was taken as 0.80-inch and a uniform wall thickness was assumed.

4. Allowable working stresses were taken as one-half the yield strength at 600 F for all the materials considered as long as this stress figure was lower than that to cause a creep rate of 10^{-5} in/in/hr.

   The working stress assumed on this basis was well below the creep strength for all the materials except the Al-6 per cent Mg alloys. Knowledge that strengths are not impaired by irradiation and that creep rates are not increased support this as a reasonable assumption.

5. Wall thicknesses were calculated using the equation:

$$\sigma_\theta = \frac{P_1 (a^2 + b^2)}{b^2 - a^2}$$

where:

σ_θ = maximum circumferential tensile stress, psi

P_1 = internal pressure, psi

a = inner radius-inches (0.80 inch)

b = outer radius-inches

The working stresses and wall thicknesses calculated for the materials are shown below.

Material	Working Stress psi	Minimum Wall Thickness-inches
Bureau of Mines Zr	5000	0.290
Zircaloy-2 Beta annealed	8000	0.165
Zircaloy-2 Beta Quenched alpha annealed	14500	0.090
347 stainless steel	16000	0.085
SAP (7.8% Al_2O_3)	7250	0.187
SAP (16.5% Al_2O_3)	10500	0.125
Al-6% Mg, A54S0 and 2S-Al		

APPENDIX II

THERMAL UTILIZATION FACTORS

f = thermal utilization

Σ = Macroscopic cross sections cm^{-1}

Σ_g(graphite) = $3.278 \cdot 10^{-4}$

Σ_{H_2O} (water) = 0.175

Σ_u(uranium) = 0.354

Σ_{347}(347SS) = 0.23

Σ_{SAP} = 0.010

Σ_{2S} (2S Al) = 0.012

Σ_{Zr} (Zr + 100 ppm Hf) = 0.0080

Σ_{Zr-2} (Zircaloy-2 + 100 ppm Hf) = 0.0084

$q_{graphite}$ = q_g = 1

q_{H_2O} = 20

V = cross sections of area constituents

V_{H2O} = 3.4196 cm^2

V_g = 338.40 cm^2

V_{tube} = 7.66 cm^2 (Al and Zr)

V_{tube} = 3.64 cm^2 (347 SS)

V_{jacket} = 1.431 cm^2 (0.050-inch Al)

V_{jacket} = 0.847 cm^2 (0.030-inch Zr)

V_{jacket} = 0.418 cm^2 (0.015-inch Zr)

r = r_0 = slug radius = 1.727 cm

k_u - Kappa uranium = 0.77 cm^{-1}

k_{H_2O} - Kappa H_2O = 0.35088 cm^{-1}

k_g - Kappa graphite = 0.01908 cm^{-1}

APPENDIX II

THERMAL UTILIZATION FACTORS

t = width of water annulus = 0.291 cm

b_g = external radius of graphite lattice = 10.747 cm

C_g = radius of hole in graphite lattice = 2.79 cm

F = 1.21

$(E-1)$ = 0.015

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